Theoretical study of the structural dependence of nuclear quadrupole frequencies in high-T_c superconductors

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The remarkable difference between the nuclear quadrupole frequencies ν_Q of Cu(1) and Cu(2) in $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$ is analyzed. We calculate the ionic contribution to the electric field gradients and estimate, by using experimental results for Cu_2O and La_2CuO_4, the contribution of the d valence electrons. Thus, we determine ν_{Q1}, ν_{Q2}, and the asymmetry parameter η for $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$. The number of holes in the Cu-O planes and chains is found to be important for the different behavior of ν_{Q1} and ν_{Q2}.

Nuclear quadrupole resonance (NQR) can give important information about the electronic structure of solids, since the nuclear quadrupole coupling constant is proportional to the total electric field gradient (q_{ij}) at the nucleus. An interpretation of the experimental data within a simple electronic physical picture is possible. However, in general and especially for complex systems, a quantitative analysis is difficult. Many NQR experiments have been performed for the various high-T_c compounds, and particularly for both copper sites Cu(1) and Cu(2) in $YBa_2Cu_3O_{7-\delta}$.[1-6] Obviously, different charge configurations expected in such systems may be reflected in NQR results. However, due to the complicated structure of high-T_c materials, it remains difficult to obtain from the values of the NQR frequencies ν_Q (and consequently of the total field gradient q_{ij}) for Cu(1) and Cu(2) a complete understanding of the ionic charge distribution. Furthermore, it is by no means clear whether such high-T_c materials can be treated as dominantly ionic in character and that the covalent character of the Cu—O bonds may be neglected.

Experimental results for antiferromagnetic $YBa_2Cu_3O_6$ show[7] an inversion of the magnitudes of ν_{Q1} and ν_{Q2}, which refer to Cu(1) and Cu(2), respectively, with respect to these values in $YBa_2Cu_3O_7$. One observes $\nu_{Q1}=30.11$ MHz and $\nu_{Q2}=22.87$ MHz in $YBa_2Cu_3O_6$,[7] and $\nu_{Q1}=22$ MHz and $\nu_{Q2}=31.5$ MHz in $YBa_2Cu_3O_7$.[4-6] This interesting difference could suggest that ν_Q is a sensitive quantity reflecting changes in the electronic properties of both compounds (whose crystal structures are similar). The purpose of our analysis is to estimate the quadrupole frequencies in $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$ and to explain the experimental results. We use simple assumptions about the electronic structure and consider explicity the existence of covalent Cu—O bonds. Furthermore, for determining the valence electron contribution to the electric field gradient q_{ij} we use experimental results for Cu_2O and La_2CuO_4.

The quadrupole frequency for the ^{63}Cu nucleus (with nuclear spin $I=\frac{3}{2}$) is given by

$$\nu_Q=\tfrac{1}{2}e^2Qq_{zz}^{\text{tot}}(1+\eta^2/3)^{1/2}\,, \tag{1}$$

where Q is the nuclear quadrupole moment, q_{zz}^{tot} the largest component (z component) of the total field gradient tensor in a set of principal axes, and $\eta=(q_{xx}-q_{yy})/q_{zz}$ refers to the asymmetry parameter. From a general expression of q_{zz}^{tot} as a function of the coordinates of all the nuclei and electrons in the solid[8] one can derive an approximate expression,[9] in which the sources of the electric field gradient at a certain nucleus are the outer (or valence) electrons with aspherical wave functions and the other ions (considered in lowest approximation as an infinite arrangement of point charges). Then, if the principal axes of both ionic and valence contributions are the same, Eq. (1) may be rewritten as

$$\nu_Q=[\tfrac{1}{2}e^2Q(1-\gamma_\infty)q_{zz}^{\text{ionic}}+q_{\text{val}}](1+\eta^2/3)^{1/2}\,, \tag{2}$$

where γ_∞ refers to the Sternheimer antishielding factor,[10] which accounts for the contribution from the distortion of the Cu ion both by the local field gradient and by the quadrupolar field of the nucleus. The contribution to the field gradients due to the ionic lattice is given by the term

$$\tfrac{1}{2}e^2Q(1-\gamma_\infty)q_{zz}^{\text{ionic}}\,,$$

and the term

$$q_{\text{val}}=\tfrac{1}{2}(1-R)e^2Qq_{zz}^{\text{val}}$$

refers to the field gradients produced by the valence electrons at the Cu sites, in which the shielding factor R describes the shielding by core electrons.[10] The asymmetry parameter η is written as

$$\eta=(q_{xx}^T-q_{yy}^T)/q_{zz}^T\,,$$

where

$$q_{ii}^T=q_{ii}^{\text{ionic}}+q_{ii}^{\text{val}}\,.$$

q_{zz}^{val} results from the electrons (holes) in the open d Cu shells. In terms of the number of holes in the different d orbitals, q_{zz}^{val} may be written as

$$q_{zz}^{\rm val}=A\langle r^{-3}\rangle_{3d}[n_h(3d_{3z^2-r^2})-n_h(3d_{x^2-y^2}) -n_h(3d_{xy})+\tfrac{1}{2}n_h(3d_{xz}) -\tfrac{1}{2}n_h(3d_{yz})]\ , \qquad (3)$$

where A is a constant. In what follows we will assume that the orbitals $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$ are below the Fermi level and that consequently their contributions vanish.

Note that previously Adrian[11] has calculated ν_{Q1} and ν_{Q2} in $YBa_2Cu_3O_7$ using Eq. (2). Although his results seem to be in agreement with experiment, one should note that he makes two crude assumptions. First, he considers γ_∞ to be independent of the ionic charge and he takes $\gamma_\infty^{Cu^{2+}}=-17$, which is the calculated value[12] for Cu^+. A calculation of γ_∞ for Cu^{2+} has been carried out by Gupta *et al.*[13] and gives $\gamma_\infty^{Cu^{2+}}=-7.59$. Using this value, Adrian results are no longer close to the experimental values.[14] Furthermore, performing his calculations in $YBa_2Cu_3O_6$ one obtains values which are far away (even qualitatively) from the experimental results. Second, he assumes that only Cu^{2+} contributes to $q_{\rm val}$.

In the following we determine ν_{Q1} and ν_{Q2} and the asymmetry parameter η for $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$ from Eq. (2) by calculating directly $\frac{1}{2}e^2Qq_{zz}^{\rm ionic}$ and by estimating $q_{\rm val}$ using experimental results for Cu_2O and La_2CuO_4.

We have calculated the ionic contribution $\frac{1}{2}e^2Qq_{zz}^{\rm ionic}$ for Cu(1) and Cu(2) in both $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$ using the Evjen method[15] (to insure the convergence of the numerical summations). The following charge configurations are assumed: Y^{3+},Ba^{2+} for both compounds, and $O(2)^{2-}$,$O(3)^{2-}$,$Cu(1)^{+}Cu(2)^{2+}O(4)^{2-}$ for $YBa_2Cu_3O_6$, whereas $O(2)^{1.95-}$,$O(3)^{1.95-}$,$Cu(1)^{2.4+}$, $Cu(2)^{2.1+}$,$O(4)^{2-}$,$O(1)^{1.8-}$ for $YBa_2Cu_3O_7$. O(1) refers to the oxygen atoms along the chains, and O(4) to the oxygen atoms above and below Cu(1). Note, in the assumed charge distribution for $YBa_2Cu_3O_7$, each CuO_2 plane and the chain have 0.2 and 0.6 holes, respectively, near to the values observed in recent experiments.[16] It must be mentioned that $\frac{1}{2}e^2Qq_{zz}^{\rm ionic}$ is not very sensitive to small charge changes.[17] However, the holes will contribute to $q_{\rm val}$. The values for the $\frac{1}{2}(1-\gamma_\infty)e^2Qq_{zz}^{\rm ionic}$ and the asymmetry parameter η obtained for Cu(1) and Cu(2) in $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$ are shown in Table I. These results indicate that the ionic contribution alone cannot explain the behavior of ν_Q in $YBa_2Cu_3O_7$.

Since a first-principles calculation of $q_{\rm val}$ seems still a very complicated and not yet solved many-body problem and since we only attempt to explain qualitatively the behavior of ν_{Q1} and ν_{Q2}, we will estimate $q_{\rm val}$ for Cu using simple physical arguments and with the help of experimental data for ν_Q in the related compounds Cu_2O and La_2CuO_4.

For example, $q_{\rm val}$ for Cu(1) in $YBa_2Cu_3O_6$ may be estimated from ν_Q in Cu_2O, where copper is also in the state Cu^+. Since Cu_2O is mainly ionic[18,19] and an isolated Cu^+ is spherically symmetric, it seems reasonable to take $q_{\rm val}=0$.[20–22] Our calculation of the ionic contribution for Cu in Cu_2O gives $\frac{1}{2}e^2Qq_{zz}^{\rm ionic}=4.01$ Mhz, the z principal axis being the (1,1,1) axis. The experimental values in Cu_2O are $\nu_Q=26$ MHz, and $\eta=0$.[23] Note that, using an effective $(1-\gamma_\infty)=-6.48$, one could obtain, from our calculated value 4.01 MHz for $\frac{1}{2}e^2Qq_{zz}^{\rm ionic}$, the observed experimental value for ν_Q. In order to determine now the Cu(1) quadrupole frequency in $YBa_2Cu_3O_6$ we reason as follows. The coordination O(4)-Cu(1)-O(4) is very similar to that of Cu in Cu_2O. The only difference is given by the interatomic distances, namely the Cu-O distance is 1.84 Å for Cu_2O,[24] whereas the Cu(1)-O(4) distance for $YBa_2Cu_3O_6$ (Ref. 25) is 1.79 Å. Since this change in the interatomic distances is relatively small

TABLE I. Calculated results for the field gradient contribution $\frac{1}{2}e^2Q(1-\gamma_\infty)q_{zz}^{\rm ionic}$ of the lattice and the asymmetry parameter η. The Cu d-electron field gradient contribution $q_{\rm val}$ is estimated from experimental results for the NQR resonance frequency ν_Q in Cu_2O and La_2CuO_4; modifications due to changes in covalency, see discussion in text, are included. Results for $q_{\rm val}$ given in brackets follow if values derived for La_2CuO_4 are used.

	$YBa_2Cu_3O_6$	$YBa_2Cu_3O_7$
$\frac{1}{2}e^2Qq_{zz}^{\rm ionic}$(Cu(1))	4.86 MHz	−32.36 MHz
$\frac{1}{2}e^2Q(1-\gamma_\infty)q_{zz}^{\rm ionic}$(Cu(2))	−22.5 MHz	−18.9 MHz
$q_{\rm val}$(Cu(1))	0.0 MHz	52.1 MHz
$q_{\rm val}$(Cu(2))	45.4 MHz (52.1 MHz)	47.1 MHz
η_1	0.0	0.67
$\eta_1^{\rm expt}$	0.0	~1.0
η_2	0.0	0.07
$\eta_2^{\rm expt}$	0.0	0.01–0.1
ν_{Q1}	31.5 MHz	21.2 MHz
$\nu_{Q1}^{\rm expt}$	30.11 MHz	22.0 MHz
ν_{Q2}	22.87 (29.6) MHz	28.0 MHz
$\nu_{Q2}^{\rm expt}$	22.87 MHz	31.5 MHz

and the distance to the planes is still large,[25] we assume that the covalent contribution (due to the q_{val}) to ν_{Q1} is small. Then, if the antishielding factor is the same in both compounds, then we can write

$$\nu_{Q1} \simeq \nu_Q(Cu_2O) q_{zz}^{ionic}(YBa_2Cu_3O_6)/q_{zz}^{ionic}(Cu_2O) .$$

Our calculated value for $\frac{1}{2}e^2Qq_{zz}^{ionic}$ in $YBa_2Cu_3O_6$ is 4.86 MHz (where the z principal axis is the c axis). Then, ν_{Q1}=31.5 MHz (expt: 30.11 MHz). Note that this value might be smaller if a small amount of holes is present in the $3d_{3z^2-r^2}$ orbital of Cu(1).

In order to estimate q_{val} and ν_Q for the other Cu atoms in $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$, we use experimental data for Cu^{2+}. Recently, NQR measurements have been performed on the $La_2CuO_{4-\delta}$ compound,[26] where Cu is approximately Cu^{2+}. The quadrupole frequency for Cu was observed to be ν_Q=31.9 MHz. Our calculation yields

$$\tfrac{1}{2}e^2Qq_{zz}^{ionic} = -2.35 \text{ MHz}$$

for this compound. Then, using $\gamma_\infty^{Cu^{2+}} = -7.59$,[13] we derive from Eq. (2) q_{val}=52.1 MHz. Taking into account that the z principal axis is the c axis, and that the quadrupole moment is negative [$Q(^{63}Cu) = -0.211$ b (Ref. 27)], it is possible to understand, from Eq. (3), the positive value of q_{val} as resulting from holes in the $3d_{x^2-y^2}$ orbital of Cu. If the number of holes were $n_h = 1$, then Cu would be in a pure Cu^{2+} state and one would calculate according to Adrian[11] q_{val}=95.5 MHz. The smaller value q_{val}=52.1 MHz derived by us indicates stronger covalent bonding. If we assume that Cu(2) in $YBa_2Cu_3O_6$ has nearly the same configuration as Cu in La_2CuO_4, and thus insert q_{val}=52.1 MHz and our calculated value for $YBa_2Cu_3O_6$ of

$$\tfrac{1}{2}e^2Qq_{zz}^{ionic} = -2.62 \text{ MHz}$$

in Eq. (2), we obtain

$$\nu_{Q2}(YBa_2Cu_3O_6) \simeq 29.6 \text{ MHz} .$$

This is somewhat larger than the experimental value 22.87 MHz. However, there are structural differences between La_2CuO_4 and $YBa_2Cu_3O_6$. The oxygen atoms above and below Cu(2) along the c axis have different coordinations. In La_2CuO_4 this type of oxygen lies between Cu(2) and La, whereas in $YBa_2Cu_3O_6$ it is located between Cu(2) and Cu(1) [closer to Cu(1) than to Cu(2)]. Furthermore, in the case of the La compound, the oxygen atoms are rather O^{2-}, because they have only the possibility to make covalent bonding with Cu, which is 2.4 Å away. In the $YBa_2Cu_3O_6$ the O(4) may form at least weak bonds with the Cu neighbors [Cu(1) and Cu(2)], through the hopping matrix elements between p_z orbital of O(4) and the $3d_{3z^2-r^2}$ orbitals of the Cu atoms. This would favor the existence of holes in these orbitals (which in the ionic picture are assumed to be absent). Hence, with respect to La_2CuO_4, more itinerancy is expected for $YBa_2Cu_3O_6$ along the c axis with consequent gain of kinetic energy. A resultant smaller number of holes in the $3d_{3z^2-r^2}$ orbital of Cu(2) in $YBa_2Cu_3O_6$ will reduce the value for q_{val} (because it has negative contribution).

Since the q_{val} due to one hole in the $3d_{3z^2-r^2}$ is opposite to q_{val} produced by one hole in the $3d_{x^2-y^2}$, we can use the value $q_{val}(3d_{x^2-y^2})$=95.5 MHz [$=-q_{zz}^{val}(3d_{3z^2-r^2})$] for Cu^{2+}, as calculated by Adrian[11] using Hartree-Fock orbitals, to estimate the number of holes in the $3d_{3z^2-r^2}$ of Cu(2) needed to reduce ν_{Q2} from the calculated value 29.6 MHz to 22.87 MHz. We obtain $n_h(3d_{3z^2-r^2})$=0.07 holes more than in La_2CuO_4. Actually, a decrease of the number of holes in the $3d_{x^2-y^2}$ can also be responsible for a reduction of ν_{Q1} [see Eq. (2)]. Hence, the relevant quantity which changes with respect to La_2CuO_4 is

$$\Delta = n_h(3d_{x^2-y^2}) - n_h(3d_{3z^2-r^2}) ,$$

and thus,

$$\Delta(YBa_2Cu_3O_6) = \Delta(La_2CuO_4) - 0.07$$

should hold for Cu(2) in $YBa_2Cu_3O_6$ in order to obtain agreement with experiment. This indicates that ν_Q depends sensitively on the d-hole distribution. Note that this is also supported by NQR measurements on Cu in the superconducting[28] $(La_{0.925}Sr_{0.075})_2CuO_4$ yielding ν_Q=35.3 MHz. This compound has 0.15 extra holes in the CuO_2 plane as compared with La_2CuO_4. Some of these holes are at the Cu atom, and mainly in the $3d_{x^2-y^2}$ orbital. Consequently, q_{val} increases and thus ν_Q explaining the experimentally observed increase in ν_Q with respect to the undoped compound.

We now analyze the NQR results for Cu(2) in the $YBa_2Cu_3O_7$ compound, taking into account that the distance between Cu(2) and O(4) is $r^{(1)}$=2.28 Å, smaller than in $YBa_2Cu_3O_6$, where $r^{(0)}$=2.46 Å.[25] Thus, Cu(2) in $YBa_2Cu_3O_7$ will have stronger covalent bonding with O(4) than Cu(2) in $YBa_2Cu_3O_6$ and consequently the increase in the number of holes in the $3d_{3z^2-r^2}$ orbital with respect to La_2CuO_4 will be larger than for $YBa_2Cu_3O_6$, since the hopping matrix element $V_{pd\sigma}$ between this orbital and the p_z orbital of O(4) is larger. We can roughly estimate for both compounds the number of holes in the $3d_{3z^2-r^2}$ of Cu(2) due to the covalent bonding with the p_z orbital of O(4) as given by $n_h \sim [V_{pd\sigma}/(\epsilon_d - \epsilon_p)]^2$, where ϵ_d, ϵ_p are the on-site energies of both orbitals. Thus, the rate

$$\rho \equiv n_h^{(0)}(3d_{3z^2-r^2})/n_h^{(1)}(3d_{3z^2-r^2}) ,$$

where index 0 and 1 refer to $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$, respectively, is given by

$$\rho \simeq (V_{pd\sigma}^{YBa_2Cu_3O_7}/V_{pd\sigma}^{YBa_2Cu_3O_6})^2 .$$

Using the distance dependence of the hopping element $V_{pd\sigma} \sim r^{-7/2}$, derived by Harrison,[29] and inserting the maximum value for $n_h^{(0)}(3d_{3z^2-r^2})$=0.07 holes estimated before, we obtain approximately

$$n_h^{(1)}(3d_{3z^2-r^2}) = n_h^{(0)}(3d_{3z^2-r^2})(r^{(1)}/r^{(0)})^{-7}$$
$$= 0.12$$

with respect to the $n_h(3d_{3z^2-r^2})$ in La_2CuO_4. There will also be a difference between the number of holes in the orbital $3d_{x^2-y^2}$ of Cu in the planes for La_2CuO_4 and $YBa_2Cu_3O_7$. This difference cannot be estimated in the same way as for the $3d_{3z^2-r^2}$ orbital, since the orbital $3d_{x^2-y^2}$ of Cu(2) has only vanishing hopping elements with O(4). Thus, we obtain a maximum value for

$$\Delta(YBa_2Cu_3O_7) = n_h^{(1)}(3d_{x^2-y^2}) - n_h^{(1)}(3d_{3z^2-r^2}) ,$$

namely,

$$\Delta(YBa_2Cu_3O_7) = \Delta(La_2CuO_4) - 0.12 .$$

This would imply a reduction of $q_{val} = -52.1$ by 11 MHz, at most, upon going from La_2CuO_4 to $YBa_2Cu_3O_7$. However, the latter high-T_c superconductor has more holes, namely $n_h \sim 0.25$ holes in the CuO_2 planes,[16] which so far are not included in our analysis. If we make the assumption that these holes are distributed among the Cu(2) and the two oxygen atoms in the same proportion as in $(La_{0.925}Sr_{0.075})_2CuO_4$, in which the 0.15 holes in the plane produce a frequency increase of 3.4 MHz, this will lead (using a linear interpolation) to an increase of q_{val} by 6 MHz. Hence, q_{val} for Cu(2) in $YBa_2Cu_3O_7$ will be smaller than for Cu in La_2CuO_4 by ~ 5 Mhz. Thus, if we use our calculated value for

$$\tfrac{1}{2}e^2Q(1-\gamma_\infty)q_{zz}^{\text{ionic}} = -18.9 \text{ MHz}$$

for $YBa_2Cu_3O_7$ and

$$q_{val} = (52.1-5) \text{ MHz} = 47.1 \text{ MHz}$$

we obtain $\nu_{Q2} \simeq 28$ MHz. The discrepancy with the experimental value of $\nu_{Q2} = 31.5$ MHz is reasonable.

To determine ν_{Q1} in $YBa_2Cu_3O_7$, we note that Cu(1) has covalent bonds with its four neighboring oxygen atoms within the *yz* plane. The atomic environment is approximately similar to that of Cu in La_2CuO_4 (since the other two of the six oxygen neighbors are farther away). Using then $q_{val} = 52.1$ MHz as derived for La_2CuO_4, and our calculated values for

$$\tfrac{1}{2}e^2Q(1-\gamma_\infty)q_{zz}^{\text{ionic}} = -32.36 \text{ MHz}$$

and for η,[30] we obtain $\nu_{Q1} = 21.2$ MHz. This is in good agreement with experiment. However, on physical grounds one expects q_{val} in $YBa_2Cu_3O_7$ to be larger than in La_2CuO_4 since, in $YBa_2Cu_3O_7$, Cu(1) is in the $Cu^{2.4+}$ state.[31] Distributing the holes equally among the $3d_{y^2-z^2}$ and the $3d_{3x^2-r^2}$ orbitals might change q_{val} only slightly (the two orbitals contribute with opposite signs). The discrepancy between our calculated value of η_1 and the experimental η_1 for $YBa_2Cu_3O_7$ is probably due to the different electronic density at O(1) and O(4). This has a strong effect on the asymmetry parameter, but not on the quadrupole frequency.[17] This means that η must be calculated more accurately including the effect of the *p* orbitals of the neighboring oxygen atoms.

Our results for ν_Q and the asymmetry parameter η obtained by calculating $\frac{1}{2}e^2Qq_{zz}^{\text{ionic}}$ and using Eq. (2) are summarized in Table I. Note that we calculated $\frac{1}{2}e^2Qq_{zz}^{\text{ionic}}$ for a crystal consisting of point charges and estimated q_{val} from experimental results for Cu_2O and La_2CuO_4. As discussed the results for ν_{Q1}, ν_{Q2} depend sensitively on the hole distribution. ν_Q could even be a good measure of the number of holes in the CuO_2 planes. But for a precise analysis γ_∞ remains a problem. Note that taking different values of γ_∞ can change the results dramatically.[14] Therefore, the use of higher-order terms than those of Eq. (2) in the expression of the quadrupole frequency makes no sense.

It is of interest to note that charge fluctuations on Cu and O sites need not be considered explicity to explain experimental results. NQR experiments on $YBa_2Cu_3O_{7-\delta}$ as a function of δ and Ga and Zn doping [which has interesting influence on T_c (Ref. 32)] could give further useful information.

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[30]We have assumed $q_{xx}^{\text{val}}=q_{yy}^{\text{val}}=q_{zz}^{\text{val}}/2$, since the nonionic contribution to the field gradients is due to d electrons with equal charge density along the x and y principal axes.

[31]We have used as antishielding factor for Cu(1) in $YBa_2Cu_3O_7$ $(Cu^{2,4+})$ the quantity $\gamma_\infty=x\gamma_\infty^{Cu^{2+}}+(1-x)\gamma_\infty^{Cu^{3+}}$, where $x=0.6$ is the concentration of Cu^{2+} in $Cu^{2,4+}$, $\gamma_\infty^{Cu^{2+}}=-7.59$, and $\gamma_\infty^{Cu^{3+}}=-7.04$ (see Ref. 11).

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